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Abstracts of Forthcoming Articles

New Pyrochlores of the Charge-Coupled Type. R. A. McCauley and F. A. Hummel. Department of Ceramics, College of Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854.
For $A^{2+}A^{4+}Ti_2O_7$-type compositions, it was found that an upper limit of 0.23 Å for the size difference of the A cations existed for pyrochlore formation. Pyrochlores of the $A^{1+}A^{3+}Ta_2O_7$ type could not be formed. Although pyrochlores of the $A_2^{1+}B_2^{6+}O_7$ type could not be prepared, pyrochlores of the type $A^{1+}A^{3+}B^{4+}B^{6+}O_7$ could be prepared. Compositions of the type $Ca_xGd_{2-x}Sn_{2-x}Sb_xO_7$ ($x = 0$ to 1) showed that the pyrochlore structure could form partial crystalline solutions with compositions of the weberite structure.

Superconductivity of Some Transition Metal Compounds. A. Norlund Christensen, S. E. Rasmussen, and G. Thirup. Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark.
Single crystals of niobium carbonitride were made by zone melting growth methods and single crystals of γ-NbN and δ-NbN by zone annealing crystal growth. The crystals are nonstoichiometric in contrast to the niobium carbonitride or niobium nitride prepared in reaction with nitrogen gas and niobium–niobium carbide mixtures and niobium metal, respectively. The transition temperature for superconductivity (T_c) decreases with increasing deviation from stoichiometry, and a determination of T_c is a nondestructive determination of this deviation. An instrument using the Wheatstone bridge principle is described and T_c values are listed for some nonstoichiometric single crystals of niobium carbonitride and niobium nitride.

Calorimetric Investigation of the Ferroelectric $\bar{4}3m$–$mm2$ Phase Transition in Boracite Crystals. M. Delfino, G. M. Loiacono, W. A. Smith, and P. S. Gentile. Philips Laboratories, Briarcliff Manor, New York 10510.
The isobaric molar heat capacity of Cr–Cl, Fe–I, Cu–Cl, Ni–Br, and Zn–Br boracite at the ferroelectric $\bar{4}3m$–$mm2$ phase transition is reported. The magnitude of the rise in C_p at the transition, and the large upper bound values of ΔH and ΔS prove that the phase transition is first order. The values of ΔH follow the trend Zn–Br $\gg$ Ni–Br $>$ Cr–Cl $\gg$ Cu–Cl $>$ Fe–I, reflecting possible structural dissimilarities among the boracites. Thermal annealing of single-crystal boracite samples of Ni–Br and Cr–Cl is found to remove multiple peaking of the heat capacity at the transition resulting in single-peak heat capacity curves. The multiple peaking is thought to arise from internal stresses within the crystal.

Intergrowth in Complex Bismuth Oxides, $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$ ($n = 5 \sim 8$), Revealed by 1-MV High-Resolution Electron Microscopy. Shigeo Horiuchi, Kunitaka Muramatsu, and Masaji Shimazu. National Institute for Research in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki, 300-31 Japan.
A complex bismuth oxide crystal, prepared by heating powders with a nominal composition $Bi_2CaNb_2O_9 \cdot 4NaNbO_3$, is composed of several phases, $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$, mainly with $n = 5$ to 8. One-megavolt high-resolution electron microscopy reveals that the structure of each phase is constructed by perovskite-like layers interleaved with Bi_2O_2 sheets. One of these phases grows only in limited regions, in which other phases with different values of n intergrow very finely. This causes a characteristic intensity profile on the diffraction pattern. Experimental evidence on the reaction of the crystal with water is presented.

The structure of the 27-Layer Polytype of $BaCrO_3$. Paul S. Haradem, Bertrand L. Chamberland, and Lewis Katz. Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268.

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Twenty-seven-layer barium chromium oxide, $BaCrO_3$, was prepared at 1200°C and 60–65 kbar by reaction of CrO_2 and Ba_2CrO_4. The compound crystallizes in space group $R\bar{3}m$ with hexagonal cell dimensions $a = 5.652 \pm 0.002$ Å, $c = 62.75 \pm 0.02$ Å. The structure was determined from 1070 independent reflections, of which 811 were considered observed, collected by automated counter methods and refined by least-squares methods to a conventional R value of 4.1%. The structure consists of a 27-layer stacking sequence of close-packed BaO_3 layers, Zhdanov notation for the sequence (3)2(2)2, with all of the O_6 octahedral sites occupied by Cr. Strings of four pairs of face-sharing octahedra in which the pairs are linked to each other by corner sharing are in turn joined to each other by octahedra sharing only corners. The structure is thus closely related to the four-layer and six-layer polytypes of $BaCrO_3$. Bariums in two of the five crystallographic positions showed large thermal anisotropy and are better described in terms of half-atom occupancy in split sites.

Neutron Diffraction Experiments on $CsCrI_3$ at 300, 77, and 1.2°K. H. W. ZANDBERGEN AND D. J. W. IJDO. Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands.
$CsCrI_3$ has been investigated by neutron powder diffraction at room temperature, 77°K, and 1.2°K. It undergoes a phase transition at 150°K due to the cooperative Jahn–Teller effect. The high-temperature form, α-$CsCrI_3$ (hexagonal, space group $P6_3/mmc$, $a = 8.127(1)$ Å, $c = 6.944(1)$ Å, $Z = 2$), adopts the $BaNiO_3$ structure with a local Jahn–Teller distortion. The low-temperature form β-$CsCrI_3$ (orthorhombic, space group $Pbcn$, $a = 8.102(1)$ Å, $b = 13.792(1)$ Å, $c = 6.900(1)$ Å, $Z = 4$), has a structure not yet reported for a Jahn–Teller distorted $BaNiO_3$ structure. It is shown that the low-temperature form can be derived from the $BaNiO_3$ structure by means of canting of triangles, formed by the three common I^- ions of two adjacent CrI_6^{4-} octahedra. The magnetic structure of β-$CsCrI_3$ at 1.2°K is found to consist of an antiparallel sequence of ferromagnetic (001) planes with a magnetic moment in the |100| direction of 3.26 μ_B.

X-Ray Study of the Ordering of the Alkali Ions in the Intercalation Compounds Na_xTiS_2 and Li_xTiS_2. TJIPKE HIBMA. Brown Boveri Research Center, CH-5405 Baden-Dättwil, Switzerland.
The arrangement of the alkali ions in electrochemically intercalated TiS_2 crystals was studied by diffuse X-ray techniques. In Na_xTiS_2 a stage 3 phase was discovered in addition to the known stage 1 and 2 phases. Three types of three-dimensionally ordered superstructures were observed: a $(3^{1/2} \times 3^{1/2})$ superstructure for stage 2 and 3 phases, a (2×2) and a $(2 \times 3^{1/2})$ superstructure for stage 1 and 2 phases. The appearance of these superstructures is consistent with a screened Coulomb interaction between the sodium ions. In the single-phase region above $x = \frac{1}{2}$, diffuse rings show up in addition to the $(2 \times 3^{1/2})$ superlattice. These rings are caused by local rearrangements of the ions to accomodate the excess sodium ions. The $(3^{1/2} \times 3^{1/2})$ and (2×2) superstructures were also observed in Li_xTiS_2 crystals.

Studies of Layered Uranium(VI) Compounds. III. Structural Investigations of Hydrogen Uranyl Phosphate and Arsenate Tetrahydrates below the Respective Transition Temperatures of 274 and 301°K. MARK G. SHILTON AND ARTHUR T. HOWE. Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, England.
The layered hydrates $HUO_2PO_4 \cdot 4H_2O$ (HUP), and $HUO_2AsO_4 \cdot 4H_2O$ (HUAs), which are proton-conducting solid electrolytes above the conductivity transitions at 274 and 301°K respectively, have been shown, using powder X-ray diffraction, to change from tetragonal to orthorhombic symmetry below these temperatures. For HUP the unit-cell dimensions were $a = 6.985(5)$ and $c = 17.45(1)$ Å at 290°K, and $a = 6.966(5)$, $b = 7.004(5)$, and $c = 17.43(1)$ Å at 260°K. The values for HUAs were $a = 7.150(2)$ and $c = 17.608(5)$ Å at 305°K, and $a = 7.128(2)$, $b = 7.168(2)$, and $c = 17.613(5)$ Å at 293°K. The enthalpies of these displacive-type transitions were found from differential scanning calorimetry to be less than 0.5 kJ per mole of water for both compounds. Such a small value indicates that the rigid-like water lattices existing below the transitions do not become liquid-like above the transitions. The infrared spectra of HUP and HUAs both above the transitions and down to 80°K showed clear evidence of the presence of H_3O^+ ions, showing that the conductivity transitions are not caused by a loss of carriers. Rather, the antiferroelectric ordering, known to exist for HUAs, would appear to cause the conductivity drop. Upon this indication of ordering within the water layers, two possible related H-bond ordered structures have